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Coumarin end-capped polystyrene by ATRP and photodimerization reaction

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Summary

New coumarin-end-capped polystyrenes have been prepared using functional initiators by atom-transfer radical polymerization (ATRP). In the first case, the photosensitive initiator, 7-chloroacetoxy-4-methyl-coumarin, was prepared. Then the styrene was initiated by 7-chloroacetoxy-4-methyl-coumarin in the presence of a CuBr/bipyridine. The functionalization of the polymers was nearly quantitative, the molecular weight and structure were well controlled by adjusting the monomer/initiator molar ratio, polymerization temperature and time. At high monomer conversion, the polydispersity index of polymer was about 1.40. These coumarin-end-capped polystyrenes underwent [2+2] cycloaddition reaction under UV irradiation in film state. After irradiation the molecular weight and polydispersity index of polystyrene both increased, but the maximum molecular weight was less than the double of original one. It means that the photodimerization reaction was not complete throughly in film state for the diffusion of coumarin groups was blocked by polymeric chain entanglement.

Introduction

The traditional methods for preparing end-capped polymer are anionic polymerization and chain-transfer free radical polymerization [1,2]. Although free radical polymerization can be carried out under very mild condition and nearly all monomers are suitable for the technique, the disadvantage is lack of structure controllability and low efficiency of end-functionalization. The preferred methods for preparing end-capped polymers are anionic polymerization. By this routine a well-defined polymer obtained with better control of functionality, molecular weight and polydispersity. But the anionic polymerization must carry out under very harsh conditions and needed high purity monomer and very low temperature. Not all monomers meet the demands of anionic polymerization.

Now Atom transfer free radical polymerization (ATRP) becomes very popular in preparing end-capped polymers [3]. This living/controllable free radical polymerization method not only holds nearly all the merits of traditional free radical polymerization, but also has the equal ability to control the polymer structure and molecular weight just like anionic polymerization. Two ways have been proposed to prepare the end-capped polymer by ATRP. First one is end group transformation. Azide [4], animino [5], hydroxyl [6], allyl [7] and phosphonium [8] groups have been introduced into polystyrene end by nucleophilic reaction. The second one is utilization of functional initiators. Lots of organic compounds with activated carbon-halogen (C-X) bond can be used as ATRP initiators. Hydroxyl [9], uridine and adenosine [10], acid [11], thiol [12] and allyl [13] have been successfully introduced in to polymer end by carefully selecting the corresponding initiators.

Some new functional initiators also proposed by different research groups. Pyrrole[14], Oxazoline[15], pyrene[16], single-walled carbon nanotubes[17], bipyrridine[18], aldehyde[19], N,N-dimethylaniline[20], norbornenyl[21] were used as functional initiators to prepare end-capped polymers. But little attention was paid to photosensitive initiators.

Recently we successfully designed and prepared 8-hydroxyquiniline end-capped polystyrene by ATRP and studied its chelating ability with aluminum ion, this polymeric complex showed excellent photoluminescent property in film state. In this article a photosensitive ATRP initiator, 7-chloroacetoxy-4-methyl-coumarin, was prepared and then coumarin-end-capped polystyrene was obtained by ATRP method. The resulting polymer took place photodimerization reaction in solid sate and the reaction was investigated by FTIR, absorption spectrum and molecular weight changes before and after irradiation.

Experimental

Materials

Styrene (Fisher, Pittsburgh, PA) was purified by filtering through aluminum oxide column to remove inhibitor and then stirred with calcium hydride overnight and distilled under reduced pressure. The purified styrene was kept below -5^{o}C in inert atmosphere. Cu(I)Br (Acros, Pittsburgh, PA) was purified in a glove box by stirring with glacial acetic acid and filtering to remove any traces of Cu(II). The Cu(I)Br was then washed with ethanol and kept in a glove box to protect Cu(I)Br from oxidation. 2,2'-Bipyridine (J&K Chemical LTD, Beijing) was recrystallized before use and chloroacetyl chloride was distilled under reduced pressure. Anisole (J&K Chemical LTD, Beijing), tetrahydrofuran (THF, HPLC grade, unstabilized; JT Baker, Phillipsburg, NJ) were used as received.

Instruments

FT-IR spectrum was recorded on Bruker EQUINOX 55 FTIR system. UV-Vis spectrum was recorded on Shimadzu UV-Vis 2550 and ^{1}H NMR analysis was carried out on Varian Mercury Plus-400 instrument. Samples taken from the polymerization tube for monomer conversion were analyzed through a HP 5890 gas chromatography. Anisole was used as an internal reference. The remaining samples were filtered through aluminum oxide to remove the remaining copper species. Molecular weights and molecular weight distributions were determined by gel permeation chromatograph

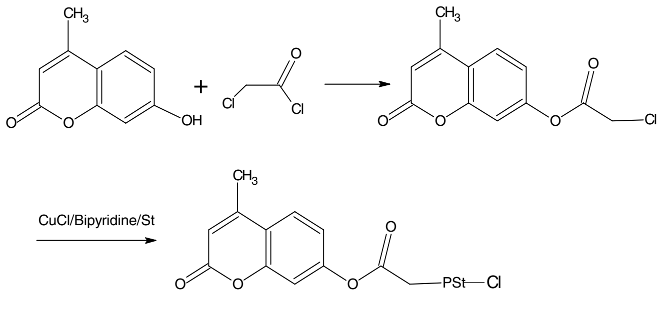
(GPC, Agilent1100 HPLC, Plgel MIXED-C type column, polystyrene standard purchased from Waters, THF as eluent).

Preparation of 7-chloroacetoxy-4-methylcoumarin [Scheme 1]

Dry pyridine (0.5ml) was slowly added to the mixture of 7-hydroxy-4-methylcoumarin (10.0g) and chloroacetyl chloride (15ml) at room temperature. After refluxing for 40min the mixture was cooled to room temperature and treated with ice water. The crude product was collected, washed with water and recrystallized from methanol as colourless needles. Yield 85.0%. m.p: 180-181^o C; ^{1}H NMR, 2.50(d, 3H, 4-Me,), 4.60(s,2H,-CH_2-,) 6.30(d, 1H, 3-H),7.19(1H, 8-H), 7.22(1H, 6-H), 7.83(1H, 5-H).

Polymerization of Styrene initiated by 7-chloroacetoxy-4-methylcoumarin

In a glove box, appropriate amounts of Cu(Ⅰ)Br and ligand were weighted into a 25ml cleaned polymerization tube which equipped with a magnetic stirring bar and sealed with a rubber septum. The tube was then taken out of the glove box, attached to a vacuum line, and cycled between vacuum and nitrogen three times. Styrene and anisole were bubbled with nitrogen for 30min just before use and then injected into the flask using degassed syringes. The flask was subjected to three freeze-pump-thaw cycles. The reaction tube was then immersed in a thermostated oil bath at 110 ^{o}C, and the mixture was stirred rapidly for 0.1h to dissolve the copper salt complex. Then weighted 7-chloroacetoxy-4-methyl- coumarin in anisole was quickly injected into the solution via a glass syringe to start the polymerization. The solution gradually turned dark green. At various time intervals, samples were taken via degassed syringes and diluted with THF and were used for measurements of monomer conversions and molecular weights.



CPSt

Scheme 1: Synthesis of initiator and polymerization of styrene by ATRP

Irradiation of the Film

High-pressure Hg lamp system (1.0 kW) equipped with an optical filter (Shengyan HB Optical Technology Company, LTD, China) was used as irradiation resource. In all cases, UV light irradiation was conducted under vacuum.

Photodimerization reaction of coumarin end-capped polypstyrene was studied in film state. Polymer (1.0g) was dissolved in dichloromethane (100ml) to get 1% (W/V) polymer solution. Then the polymer was spin-coated on a silica glass and dried in dark to a constant weight. The polymer film coated on silica was irradiated with UV light for a period of time. The photodimerization reaction was monitored with FT-IR and UV-Vis.

Results and discussion

The mechanism of ATRP has been well established by Matyjaszewski and others [22]. The relationship of $\ln\frac{[M]_0}{[M]}$ with respect to polymerization time was shown in. figure1. From it we could figure out that $\ln\frac{[M]_0}{[M]}$ increases almost linearly with polymerization time. This result indicated that the polymerization was first order kinetics and the concentration of growing radical kept constant during polymerization. At beginning of polymerization, the conversion increased rapidly and became slow after 8h polymerization. After 12h polymerization, the monomer conversion reached to 92%.

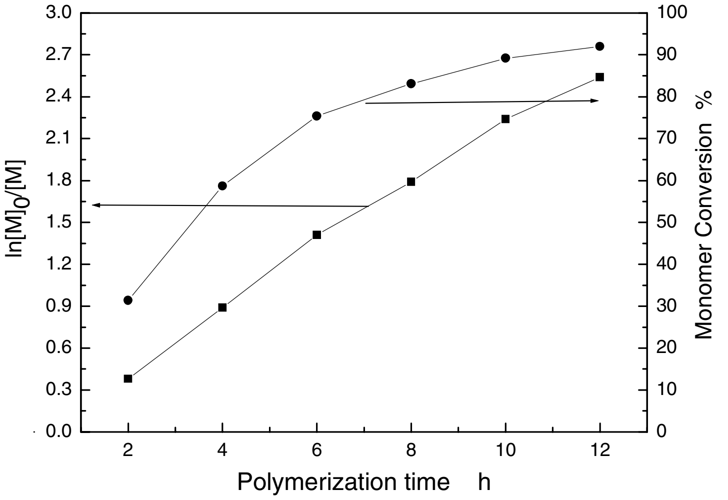


Figure 1. Kinetic plot for the polymerization of St in anisole solution (50/50,V/V) at 110°C Reaction condition: [St]/[Initiator]/[CuBr]/[Bipyridine]=100:1:1:2

The effect of monomer conversion on average molecular weight and polydispersity index was shown in figure 2. The molecular weight measured by GPC increased almost linearly with the monomer conversion. The calculated molecular weight was very close to the data from GPC. This fact indicates that this polymerization was well controlled at such polymerization condition. The polydispersity index (PDI) decreased rapidly with increasing of monomer conversion. This is typical for polymerization systems with relatively fast exchange between active and dormant species. At low monomer conversion (31.4%), the PDI value was 2.24; when the monomer conversion reached to 58.7%, the PDI value dropped to 1.61. At high monomer conversion (>75%), the PDI value was about 1.40 and didn't change much.

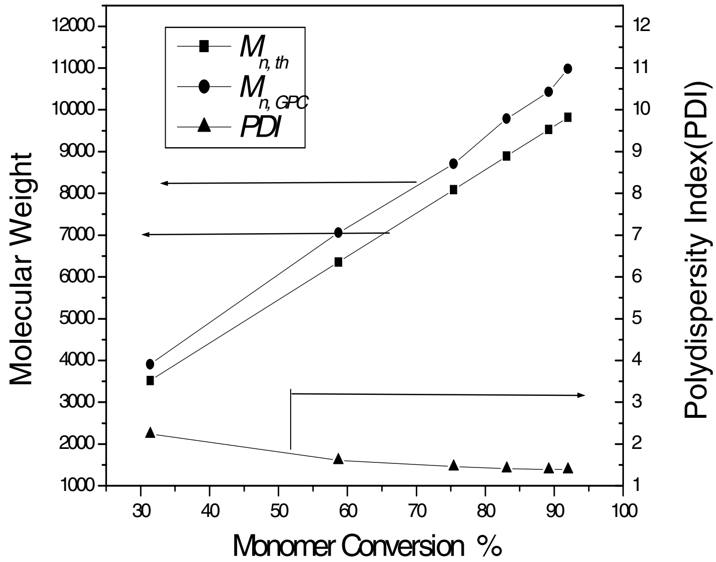


Figure 2. Monomer conversion-Molecular weight curves
Recation condition: [St]/[Initiator]/[CuBr]/[Bipyridine]=100:1:1:2, 110 °C

The effect of monomer/initiator ratio on polymerization was listed in Table 1. With the increasing of monomer/initiator ratio, the monomer conversion decreased and the number average molecular weight from GPC ($M_{n,\ GPC}$) increased. The theoretical molecular weight ($M_{n,\ th}$) was very close to the GPC results at the same polymerization time. The polydispersity index decreased with increasing of monomer/initiator ratio. The efficiency of initiator ($EI = \frac{M_{n,th}}{M_{n,GPC}}$) also decreased with increasing of monomer/initiator ratio.

The effect of polymerization temperature on monomer conversion, molecular weight, polydispersity and initiator efficiency was summarized in Table 2. With the elevation of polymerization temperature, the monomer conversion, molecular weight from GPC

Table 1: ATRP results of St initiated by 7-chloroacetoxy-4-methyl-coumarin with various monomer/initiator ratio

Entry	$[M]_0/[I]_0$	Conversion(%)	$M_{n,th}$	$M_{n,GPC}$	M_w/M_n	EI
1	25	95.2	2728	2820	1.27	0.965
2	50	92.3	5052	5600	1.29	0.901
3	75	90.2	7288	8120	1.35	0.898
4	100	89.7	9581	10420	1.39	0.919
5	125	86.4	11485	12660	1.44	0.901
6	150	84.2	13388	14730	1.47	0.909
7	175	80.6	14922	16940	1.76	0.881
8	200	75.4	15939	18830	2.03	0.846
9	225	71.6	17007	21250	2.33	0.800

[Initiator]:[CuBr]:[biPy]=1:1:2, 110°C, 8h and polydispersity index increased. Because at high polymerization temperature the dissociation of C-X bond is easier than that at lower temperature, more active species formed and initiated the polymerization to result in higher monomer conversion and molecular weight. At the same time, the Kp of reaction between of active species and monomer was increased was another important factor to result in higher monomer conversion. At high polymerization temperature, more monomer reacts with active species at one time between the transfer of active and inactive species, the wider of molecular weight distribution.

Table 2: The effect of temperature on polymerization results

Temperature °C	Monomer conversion %	$M_{n,GPC}$,	$M_{n,\,th}$	M_w/M_n	EI
90	23.7	2850	2721	1.35	0.955
100	59.9	6770	6492	1.39	0.959
110	89.7	10120	9597	1.40	0.948
120	91.2	11380	9751	1.49	0.857
130	94.7	13170	10116	2.16	0.768

Polymerization conditions: [St]/[initiator]=100:1, 8h, anisole as solvent

Characterization of Polymer

From FT-IR spectrum of purified coumarin end-capped polystyrene and pure polystyrene, we can figure out that the 1745cm^{-1} attributed to carbonyl group linking to the phenolic ring. 1711 cm^{-1} peak resulted from the carbonyl group in coumarin ring. 1600 cm^{-1} resulted from the absorption of benzyl ring. 1551cm^{-1} and 981cm^{-1} were due to the double bond in coumarin ring, and 542cm^{-1} due to the end carbon-chloride bond. 1454cm^{-1} and 1496cm^{-1} were assigned to typical C-C vibrations of polystyrene chain [23].

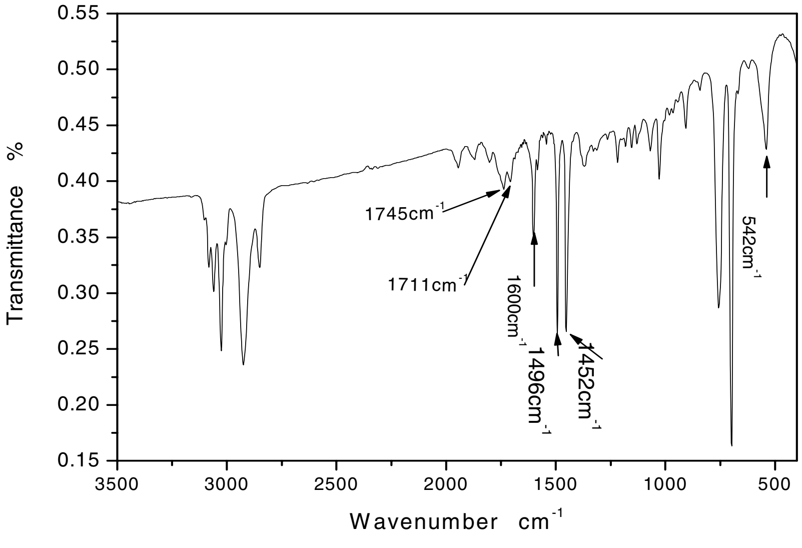


Figure 3. FT-IR spectrum of coumarin-end-capped polystyrene

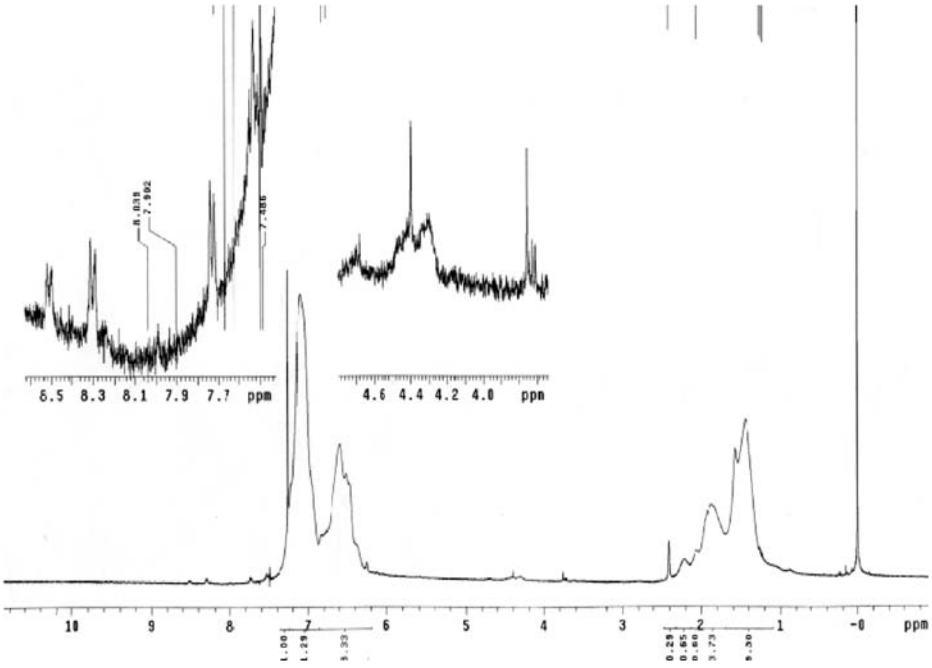
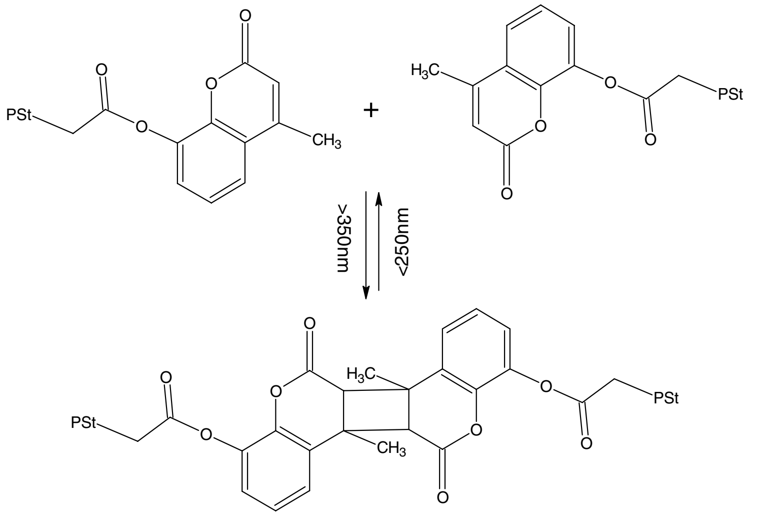


Figure 4. ^{1}H NMR spectrum of coumarin end-capped polystyrene

The NMR character of polystyrene from ATRP has been studied thoroughly by Matyjaszewski [24]. ^{1}H NMR spectrum of coumarin end-capped polystyrene was shown in figure 4. Comparing with the NMR spectrum of polystyrene initiated by Methyl 2-bromopropionate[26], we can find out that some new peaks appeared. The peaks at 8.5ppm, 8.3ppm and 7.7ppm attributed to the coumarin ring. The peak at 6.3ppm is due to hydrogen atom in double bond in coumarin ring. The peak at 4.4ppm is due to the end-methylene group linked to the chloride atom and the peak at 3.8ppm is due to the methylene group linking to the phenolic carbonyl group. The peak at 2.4ppm is due to the methyl group in coumarin ring. All these data certified that the coumarin group is chemical bonding to the polymer chain and the double bond in coumarin ring remains in its original state.

UV irradiation and photodimerization reaction

Coumarin–containing polymers have attracted many attentions for its unique properties and find applications in many high-tech fields, such as photo-cross-linkable liquid crystalline polymer, electroluminecent polymer, light and energy harvesting and biomaterials. This topic has been reviewed thoroughly by Long [25]. Photodimerization of coumarin first reported by Ciamician and Silber [26] in 1902. When the coumarin group was attached to polymer backbone, the photodomerization reaction also took place fluently. The dimer formed via the [2+2] cycloaddition reaction and resulted in a cyclobutane ring structure (Scheme 2).



Scheme 2: Photodimerization reaction of coumarin end-capped polystyrene under UV irradiation

The FT-IR spectra of coumarin-end-capped polystyrenes during UV irradiation were shown in figure 5. From Fig5A we could find that the 1711cm^{-1}-peak due to carbonyl group in coumarin ring was gradually disappeared and shifted to 1745cm^{-1}. That is because before irradiation the carbonyl group was conjugated with the double bond, so it has a absorption at lower wavenumber; after irradiation the double was reacted with each other to form a saturated cyclobutane structure, the conjugation structure was broke down and the absorption peak shifted to higher wavenumber.

The absorption peaks (1551cm^{-1} and 981cm^{-1}) due to the double band in comarin ring also decreased with the extension of irradiation time. The double was conjugated with carbonyl group, so its absorption peak appeared at low wavenumber comparing with the isolated double bond. The double bond took place intermolecular cycloaddition reaction to form saturated cyclobutane unit. With the reaction processing, the double bond was consumed and its absorption decreased. After 110min irradiation, there is a small absorption around 3450cm^{-1} which was due to carboxylic acid groups resulted from the photo-oxidation or photo-degradation of polymer during irradiation.
The cycloaddition reaction under UV irradiation was also monitored by UV-Vis absorption at 320nm. The UV-Vis spectrum of coumarin-end-capped polystyrene before and after irradiation was shown in Figure 6. The absorption peak at 320nm decreased rapidly under UV irradiation due to the disruption of aromaticity of the coumarin (Scheme2).

GPC results of coumarin end-capped polystyrene before and after irradiation were summaried in the Table3. We can figure out that the molecular weight increased with increasing of irradiation time within first 40min and then decreased for the photodegradation or photocleavage. The highest molecular weight of irradiated sample was 3610g/mol, this value was less than the double of original molecular

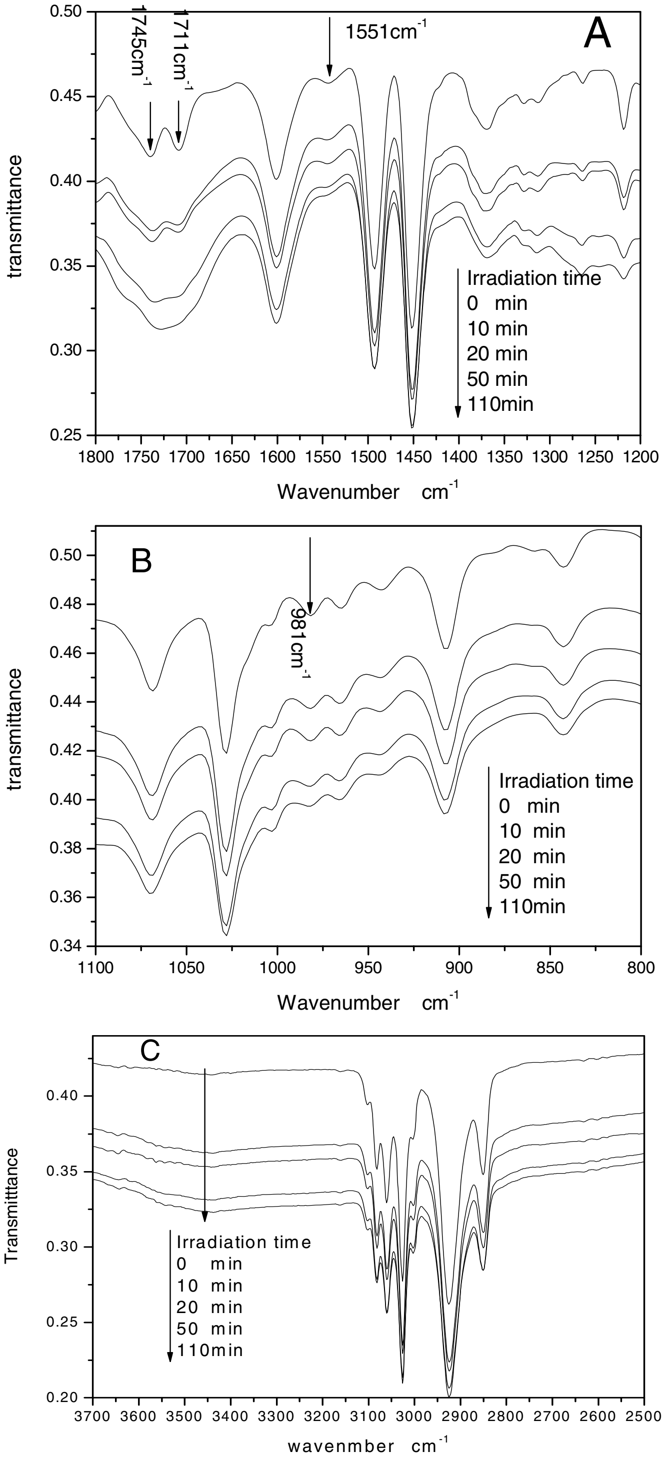


Figure 5. FT-IR spectra changes of coumarin-end-capped polystyrene under irradiation

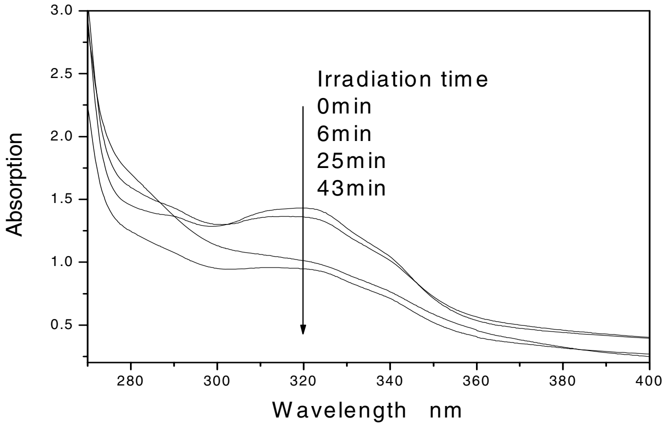


Figure 6. Absorption spectrum changes of coumarin-capped polystyrene during irradiation

weight. That means not all coumarin groups took place the photodimerization reaction because the chain movement was confined in solid state. The polydispersity index increased gradually with increasing of irradiation time.

Table 3: Effect of irradiation time on molecular weight of Coumarin-polymer

Irradiation time (min)	0	10	20	30	40	50
$M_{n,\ GPC}$	1970	2230	2550	3170	3610	3200
M_w/M_n	1.24	1.51	1.53	1.67	1.79	1.98

Conclusion

A novel photosensitive polystyrene with coumarin as end group was synthesized through atom transfer free radical polymerization with functional initiator. From the experimental results we can conclude that 7-chloroacetoxy-4-methyl-coumarin is a useful initiator of St polymerization and end-capped polystyrene is easily prepared by ATRP method. The coumarin-end–capped polymer underwent [2+2] photodimerization reaction under UV irradiation (>352nm light). But this reaction was hindered by chain entanglement in solid state and the highest molecular weight of irradiated product was less than the theoretical value. The microstructure and photodimerization reaction in solution was still under investigation.

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